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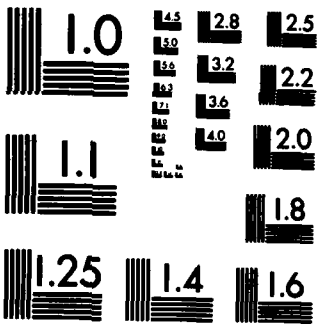

OXIDE CHARGE CHARACTERISTICS OF LOW TEMPERATURE MOS OXIDE FILMS

FINAL REPORT

S. R. BUTLER AND F. J. FEIGL

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SHERMAN FAIRCHILD CENTER FOR SOLID STATE STUDIES
LEHIGH UNIVERSITY, BETHLEHEM, PA 18015 USA

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S. R. BUTLER AND F. J. FEIGL
SHERMAN FAIRCHILD CENTER FOR SOLID STATE STUDIES
LEHIGH UNIVERSITY, BETHLEHEM, PA 18015 USA

ABSTRACT

We have studied the effects of annealing sequences on three types of silicon dioxide films fabricated at approximately 700°C. The oxide and interface charge characteristics of capacitors incorporating these oxides were measured. Results were compared with data from capacitors fabricated on a "standard" oxide film, produced by dry thermal oxidation at 1000°C. The results of these studies were as follows. (1) Deposited films obtained from the pyrolysis of tetraethoxysilane (TEOS) in low pressure nitrogen ambients exhibited very poor electrical properties. An order-of-magnitude reduction in oxide charge, interface traps, and/or bias-induced drifts was obtained by exposure of the silicon substrate to oxygen ambients before, during, or after pyrolysis. The maximum improvement also required standard N_2-PDA/PMA annealing sequences after pyrolysis. (2) Films produced by low pressure chemical vapor deposition (LPCVD) from dichlorosilane-nitrous oxide reaction required 1000°C anneals to produce as-grown charges comparable to those of the standard oxide. Even after the high temperature anneal, trapped injected charge was an order-of-magnitude larger in the deposited oxides. In the LPCVD oxides, a series of electron traps with cross sections ranging from E-17 to E-14 cm^2 were isolated. These traps were similar to traps isolated in wet thermal oxides produced above 1000°C. The dominant trapping center in the LPCVD films was systematically altered by various annealing treatments. (3) Films produced by dry high pressure thermal oxidation (HIPOX), without high temperature annealing, exhibited as-grown electrical characteristics comparable to those of the standard oxide. Charge trapping in the HIPOX films was an order-of-magnitude larger than in the standard oxide, although well prepared HIPOX films exhibited electron trapping behavior characteristic of 1000°C dry thermal oxides.

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1 STATEMENT OF THE PROBLEM STUDIED

The objective of this research was to evaluate and develop low-temperature processing sequences which improved the quality of silicon dioxide dielectric films in the 10-50 nm thickness range appropriate to very-large-scale-integration (VLSI) technology. Low fabrication temperature is a requirement which VLSI scaling imposes on insulator technology. In the present study, all oxide processing was capable of being carried out at temperatures below that required for dry thermal oxidation of silicon (i. e., below 800 °C). We purposely included some high temperature (1000°C) fabrication steps on control samples for comparison purposes. During the first two years of this program, we examined the as-fabricated electrical properties of simple capacitor structures incorporating oxide films formed on single crystal silicon substrates by low pressure chemical vapor deposition (LPCVD) and high pressure thermal oxidation (HIPOX).

The study of charge trapping associated with electron injection is a necessary component of dielectric materials characterization for microelectronic applications. This applies in particular to oxide films used as transistor gate insulators. There are device instabilities associated directly with trapping of electrons injected into MOS insulators. These include inadvertent hot electron effects in short channel transistors and the effects of intentional injection in floating gate or dual dielectric memory structures during read/write operations. In addition, dielectric breakdown, a ubiquitous problem in VLSI microelectronics, has both long-standing and recent association with current injection. During the last two years of this program, a charge trapping study was designed and executed.

Three specific low-temperature (700°C) silicon dioxide fabrication processes were studied. Each process had apparent potential for technological development. In particular, the oxide fabrication methods studied were capable of producing VLSI-scaled insulator films (10-50 nm) in reasonable times (0.1-10 hr) at low temperatures (at and below 700°C).

1. Pyrolytic decomposition of tetraethoxysilane (TEOS) at low pressures. A commonly reported method for TEOS LPCVD involves introducing liquid-source TEOS into a reactor via an inert carrier gas, commonly N_2. We have investigated this method, and a method involving an O_2 carrier. TEOS was

chosen for this investigation because it is readily available as an electronic grade liquid source material, since TEOS films are widely used for device passivation or isolation. Processing of these films is straightforward, economical, and well-documented.

2. The reaction of dichlorosilane with nitrous oxide at low pressures. This specific reaction is related to other hydride surface reactions involving similar equipment and procedures. Thus, a common basic technology is widely used to produce several microelectronic film materials (high purity, phosphorous doped, and boron doped silicon dioxide; silicon nitride; polycrystalline silicon). The dichlorosilane reaction is ordinarily used at temperatures above 700°C for LPCVD of silicon dioxide.

3. Thermal oxidation of single crystal silicon substrates by dry oxygen at high pressures (500 atmospheres). HIPOX is of particular interest since it is not a chemical deposition process. Thus, we were at once able to examine the difference between thermal oxide films and deposited oxide films at 700°C, and to examine the effect of oxidation temperature on thermal oxide films and interfaces. The latter comparison required preparation and measurement of dry high temperature (1000°C) thermal oxide films, which are the standard for gate dielectric films in microelectronics technology.

The purpose of this program was to determine the effect of specific oxide and device processing steps on the physical properties of oxide dielectric films and their interfaces with single crystal silicon. In addition to the basic LPCVD and HIPOX farication processes, the oxide film processing steps studied were the following: First, inert ambient annealing at the deposition or oxidation temperature. This is post-deposition annealing (PDA) for LPCVD or post-oxidation annealing (POA) for HIPOX. Second, annealing at low temperatures subsequent to capacitor fabrication by evaporation of high purity aluminum in vacuum. This is post-metallization annealing (PMA). The thermal oxide films prepared at 1000°C in one atmosphere of dry oxygen were given both POA treatment (at 1000°C) and PMA treatment. These films were included in the present study specifically as a benchmark "standard."

The physical properties were investigated by measurement of oxide and interface charge, using the charge and trap categories of the classification scheme proposed by Deal. These are Q_f/q, oxide fixed charge, D_{it}, interface charge trap density, and Q_{ot}/q, oxide trapped charge. Particular emphasis was placed on the development of bulk oxide trapped charge Q_{ot}/q as a result of electron current flow. Avalanche injection on p-substrate

capacitors was used to produce electron current flow in the oxide films. An automated and computer-interfaced avalanche injection and oxide charge measurement station, using primarily standard commercial instruments, was developed specifically for this program. The development of oxide charge during avalanche injection was analyzed via a first-order kinetic model describing electron current control of both bulk oxide trapping and interface trap generation.

2 SUMMARY OF THE MOST IMPORTANT RESULTS

2.1 The Quality of TEOS Pyrolytic Oxide Films

The results of bias-stress and oxide charge measurements on silicon dioxide films formed by pyrolysis of TEOS in low pressure nitrogen, oxygen, and mixed nitrogen-oxygen ambients are presented in references 1 and 2. Films deposited in a one hundred percent nitrogen ambient exhibited very poor electrical properties. This was due to the poor quality of both the LPCVD oxide bulk (manifest as a hysteretic instability exceeding one Volt in 20 nm films) and the interface between the LPCVD oxide and the silicon substrate (oxide fixed charge and interface trap charge of order E+12/cm^2).

The oxide-silicon interface was significantly improved by any one of three procedures which reduced both oxide fixed charge and interface trap charge. These procedures were:

1. *In situ* exposure of the heated silicon substrate to an oxygen ambient before LPCVD. This produced a thin thermal oxide interposed between the LPCVD oxide and the substrate.

2. The addition of oxygen to the reactor ambient during LPCVD. This probably involved surface adsorption of oxygen, which has been claimed to slow down other deposition reactions.

3. Exposure of the deposited oxide to an oxygen ambient after LPCVD. This "anneal" treatment probably involved oxidation of the imperfectly formed interface between oxide and substrate.

In addition to direct improvement of interface quality, the use of 100% oxygen ambients during pyrolysis or PDA treatment made possible further reduction in both oxide fixed charge and interface trap charge by standard nitrogen-PDA/PMA sequences. Clearly, TEOS LPCVD oxide films exposed to oxygen at the deposition temperature have a silicon dioxide-silicon interface more closely approaching that of a standard oxide film than TEOS LPCVD films exposed only to nitrogen.

The poor bulk quality of LPCVD oxide films produced by TEOS pyrolysis in a nitrogen ambient was responsible for a hysteretic bias instability. This was not significantly affected by any of the annealing sequences studied by us. However, it was reduced an order of magnitude by pyrolysis in an oxygen ambient. Neither the origin of this instability, nor its reduction, is understood.

2.2 The Quality of Hydride LPCVD Oxide Films

The results of dark current, bias-temperature-stress, and oxide charge measurements on oxide films formed by LPCVD from dichlorosilane-nitrous oxide reaction are presented in reference 3. We were primarily interested in hydride films deposited and annealed at 700°C. The best such films, given a PDA treatment in either dry nitrogen or oxygen and a standard PMA treatment, exhibited dark currents under electrical stress and as-grown oxide charge characteristics an order-of-magnitude larger than the same quantities measured in standard oxide films. However, hydride LPCVD films grown at 700°C and given both a PDA treatment at 1000°C and a PMA treatment exhibited as-grown dark current and oxide charge characteristics less than a factor-of-two greater than those of standard oxides.

Thus, our data extend the conclusions of previous workers that LPCVD oxide films produced entirely at temperatures at and below 800°C will not be suitable for gate oxide applications requiring the electrical quality of standard oxides films. A high temperature PDA step is required to attain low fixed charge and interface trap densities.

The high temperature PDA step also reduced the amount of electron trapping and interface trap generation produced by electron injection. However, hydride LPCVD films annealed at 1000°C and given a PMA treatment still exhibited oxide trapped charge and interface trap densities one order-of-magnitude greater than those measured in standard oxide films. Thus, low temperature LPCVD oxide films, even if subjected to annealing at 1000°C, may not be suitable for gate oxide applications requiring

the full electrical quality of standard oxides (in short channel devices or floating gate memories, for example).

2.3 The Quality of HIPOX Films

The results of oxide charge measurements on oxide films formed by thermal oxidation of silicon substrates in 500 atm dry oxygen are presented in reference 3. PMA treatment of HIPOX films reduced as-grown charge by more than an order-of-magnitude, and these oxides exhibited as-grown characteristics fully equivalent to those of standard oxides. Annealed HIPOX films also exhibited less oxide charge buildup during electron injection than any of the LPCVD oxide films studied. However, the HIPOX films still exhibited oxide trapped charge and interface trap densities an order-of-magnitude greater than those measured in standard oxide films.

Since all processing of the HIPOX films was at temperatures at and below 700°C, these films present a potentially significant technological advantage. Their as-grown and post-injection characteristics are superior to the best LPCVD oxides studied, and these latter films, as just noted, required a high temperature (1000°C) PDA treatment.

2.4 Oxide and Interface Electron Traps

Whenever possible, the electron injection studies were analyzed in terms of electron trapping centers in the bulk of the oxide film and donor-like electron traps in the vicinity of the silicon dioxide-silicon interface. The former were presumed to capture injected electrons, and the latter to be generated by some direct or indirect mechanism involving the injected electrons.

The present study indicated clearly that bulk oxide electron traps with four characteristic electron capture cross sections dominate the behavior of silicon dioxide films prepared under a variety of conditions. The depletion and enhancement of specific electron traps (as identified by capture cross section only) by specific sample treatments (deposition or oxidation, post-fabrication annealing, and post-metallization annealing) appears to fall into two broad categories. These two categories are typified by "wet" and "dry" types of standard high temperature thermal oxides (i. e., those produced in water containing oxidants and those produced in reasonably dry

oxygen). This comprehensive hypothesis is based on incomplete experimental information, since the capture cross section is a relatively non-discriminatory parameter for trap classification. It would be very helpful to refine the trap classification with spectroscopic studies yielding trap depths or other optical or thermal characteristics.

In summary, the hydride LPCVD oxide films contained electron trapping centers similar to those isolated in "wet" thermal oxides. The dominant trapping center in the hydride LPCVD films was systematically altered by various annealing treatments. The high quality HIPOX films described above contained electron trapping centers similar to those in "dry" oxides, and exhibited interface trap generation similar to that exhibited by "dry" thermal oxides. Neither the oxide trap nor the interface trap generation in HIPOX films was strongly affected by PMA treatment.

2.5 Summary and Conclusions

None of the oxide films produced by LPCVD at 700°C -- neither from pyrolysis of TEOS nor from dichlorosilane reaction with nitrous oxide -- approached the quality of standard gate oxide films. However, a troublesome feature of TEOS LPCVD oxide films, namely the poor quality of the oxide-silicon substrate interface, can be significantly improved if the pyrolysis is carried out or terminated in an oxygen ambient. Also, our results indicated that hydride LPCVD oxide films with as-grown characteristics equivalent to standard gate oxide films result from nitrogen annealing at 1000°C. These films may be suitable for use in practical microelectronic systems. Even with high temperature annealing, however, the efficiency and amount of charge trapping upon avalanche electron injection exceed those of standard gate oxide films by an order of magnitude. This characteristic, and the high temperature annealing requirement, may restrict their potential usefulness in VLSI or electrically alterable memory technologies.

The as-grown characteristics of low temperature HIPOX films were fully equivalent to standard gate oxide values. The HIPOX films require no high-temperature processing step, and might be useful in developing VLSI technology. However, as in the case of the LPCVD oxides, the charge trapping developed upon avalanche injection is noticeably greater than in standard gate oxide films. The trapping behavior of HIPOX films appears to be determined by well-characterized defects. These defects, and the effects of post-metallization annealing conditions on these defects, should be further investigated.

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2. R. H. Vogel, S. R. Butler, and F. J. Feigl, "Electrical Properties of 10-50 nm TEOS LPCVD Films," Manuscript for publication (Submitted to U. S. Army Research Office, 24 August 1984).

3. M. E. Zvanut, F. J. Feigl, S. R. Butler, and R. H. Vogel, "Oxide Charge Trapping in Low Temperature MOS Oxides," Manuscript for publication (Submitted to U. S. Army Research Office, 24 August 1984).

4 SCIENTIFIC PERSONNEL AND TECHNICAL ACTIVITIES

Dr. Sidney R. Butler
Professor of Metallurgy and Materials Science and Principal Investigator

Dr. Frank J. Feigl
Professor of Physics and Electrical Engineering and Co-principal Investigator

Dr. Robert H. Vogel
Research Associate

Dr. Stephen L. Titcomb
Research Assistant (received Ph. D. in Physics from Lehigh University in October, 1983)

Mr. Hongzong Chew
Research Assistant

Ms. Mary Ellen Zvanut
Research Assistant

Ms. Carole Dalmaso
Undergraduate Assistant

Mr. Leonard Trombetta
Graduate Student (supported by U. S. Army ERADCOM)

Mr. David Dutt
Undergraduate Assistant (supported by Lehigh University as a Sherman Fairchild Scholar)

The TEOS LPCVD oxide films were produced in the Microelectronic Fabrication Facility of the Sherman Fairchild Laboratory at Lehigh University. The liquid source pyrolytic reactor described in reference 2 was designed and constructed specifically for this project by Professor BUTLER and Dr. VOGEL, who together carried out the program of film deposition and device fabrication. The automated MOS capacitor measurement system described in reference 2 was also designed and constructed

specifically for this project. The development of this system, and the entire program of capacitor characterization, was carried out by Dr. VOGEL with the assistance of Dr. TITCOMB.

Overall direction of the TEOS LPCVD oxide film project was the responsibility of Professor BUTLER. Professor FEIGL was responsible for the electrical measurement program.

The dichlorosilane-nitrous oxide LPCVD oxides and the standard high temperature dry thermal oxides were also produced in the Microelectronic Fabrication Facility of the Sherman Fairchild Laboratory at Lehigh University. The design and construction of a general purpose chemical vapor deposition facility at Lehigh were in part supported by the present contract. Dr. VOGEL and Professor BUTLER participated in this development. Construction of the general facility was outside the scope of this contract, and thus is not described in detail in reference 3.

The HIPOX oxides were produced as part of a broad cooperative research program between the U. S. Army ERADCOM Device Electronics and Electronic Technology Laboratories at Ft. Monmouth, New Jersey. The high pressure oxidation chamber and the HIPOX fabrication were designed, implemented, and executed by Dr. ROBERT ZETO and coworkers of ERADCOM DELET-ED. Mr. TROMBETTA, a Lehigh Ph. D. candidate executing his dissertation as a staff member at DELET-ED, was a central participant in this effort. He was not supported by this contract.

The measurements of oxide charge and oxide charge generation in capacitors prepared on the various low temperature oxides were executed by Ms. ZVANUT. She also assumed primary responsibility for analysis and interpretation of experimental data. In this work, she was assisted by Dr. TITCOMB, Mr. CHEW, Mr. DUTT, and Ms. DALMASO. These activities were supported by the contract.

Overall direction of this project was the responsibility of Professor FEIGL. Professor BUTLER was responsible for fabrication of dichlorosilane-nitrous oxide LPCVD oxide films.

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We have studied the effects of annealing sequences on three types of silicon dioxide films fabricated at approximately 700°C. The oxide and interface charge characteristics of capacitors incorporating these oxides were measured. Results were compared with data from capacitors fabricated on a "standard" oxide film, produced by dry thermal oxidation at 1000°C. The results of these studies were as follows. (1) Deposited films obtained from the pyrolysis of tetraethoxysilane (TEOS) in low pressure nitrogen ambients exhibited very poor electrical properties. An order-of-magnitude reduction in oxide charge,

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